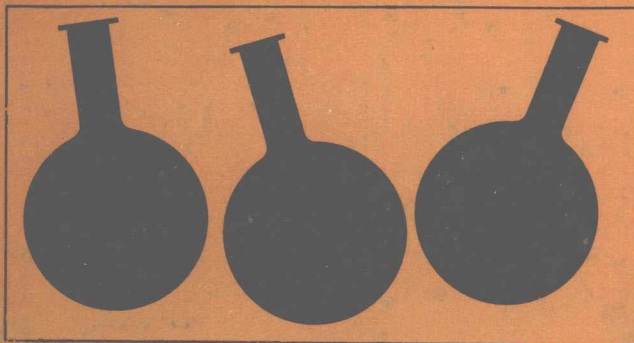# ANALYTICAL CHEMISTRY
J. G. DICK

INTERNATIONAL STUDENT EDITION

Analytical Chemistry

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INTERNATIONAL STUDENT EDITION

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Analytical Chemistry

Preface

The most obvious aim of a course in quantitative analysis is to provide the groundwork for establishing oneself as a thoroughly qualified analytical chemist. Few students pursuing undergraduate courses in quantitative analysis will have this goal in view. For these students, there is often the feeling that courses of this nature tend to make technicians of them—which is by no means the case. It should be pointed out that the primary aims of courses in quantitative analysis are:

1. To provide a fundamental knowledge of the principles underlying the techniques of quantitative analysis.
2. To provide a laboratory manipulative technique governed by the need to acquire data matching as closely as possible information previously recorded but not available to the student. The requirements of accuracy and precision here tend to stress a disciplined, orderly, and careful technique of laboratory manipulation.
3. To instill a respect for the exact data secured, and to further one's ability to evaluate such data and determine its reliability in the face of the limitations of the techniques of measurement and analysis employed.

It is worthy of note that apart from the general and far-reaching significance of the principles covered by point 1 above, points 2 and 3 are of fundamental importance in subsequent research work and day-to-day pursuits in *any* field of chemistry. With respect to undergraduate courses in chemistry, those involving quantitative analysis are often the first, and subsequently the continuing, introduction of the

student to the inexorable demands of honesty and exactitude in data accumulation and evaluation. R. S. Mulliken, a Nobel laureate in chemistry in 1966, has written the following in this connection:

> I think it was in a course in quantitative chemical analysis that an appreciation of the scientific method and its rigours began really to take hold of me. ... There were no short cuts to beat clear thinking, careful technique and endless patience. Later on, I found that the same unnatural methods are always required in those activities commonly called "research."

The tendency today in many universities to eliminate, or to absorb into other generally unrelated courses of study, the specialized and unique discipline of analytical chemistry per se can only be deplored, since it can lead eventually to nothing other than a general lowering of the ability of the research student to appreciate and to perform properly those operations associated with the accurate and precise accumulation of data.

J. G. Dick

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Introduction

1.1 ANALYTICAL CHEMISTRY

Analytical chemistry is basically the determination of the chemical composition of substances. Until recent years this was, practically speaking, the sole aim of the analytical chemist. Today, however, the field is being extended to embrace to a considerable degree the elucidation of the structural configuration of substances. It remains nevertheless a fact that in its truest sense, analytical chemistry still deals almost exclusively with the compositional aspect of substances, and it is to this aspect that the text is directed.

Analytical chemistry consists principally of two major divisions—qualitative analysis, which deals with the problem of *what* is in a substance; and quantitative analysis, which handles the problem of *how much* of each constituent is present. In the normal course of events, when preparing to analyze a substance of strictly unknown composition, qualitative analysis should precede any attempt at quantitative investigation, since the method of approach selected for the quantitative program may depend on the results of the qualitative analysis. On the other hand, where commercial work in analytical chemistry is involved, when *what* is in a substance is usually known, qualitative analysis is not generally required as a preliminary to any quantitative approach.

The techniques of qualitative analysis that were used for many years, such as in hydrogen-sulfide separations, provided an excellent opportunity to learn much concerning chemical reactions, their applicability under given circumstances, and their limitations. Such acquired information very often proved invaluable when the standard methods of quantitative analysis required modification on the basis of variations in the composition of the substances to be analyzed. In this light, one can perhaps regret the fact that such systematic procedures of qualitative analysis are now but rarely taught or used; but the modern techniques involving use of the emission spectrograph, the x-ray fluorescence spectrometer, reagents specific for many ions and molecules, etc., have provided more than adequate substitutes for the older and more conventional qualitative schemes of analysis.

Both inorganic and organic substances lend themselves to compositional investigation by quantitative analysis. Although many of the general techniques of analysis are applicable to both groups of substances, it is quite often the case that the general method of approach will differ markedly with respect to inorganic and organic substances. A full approach to the subject of quantitative analysis should undoubtedly cover both the inorganic and organic aspects. This text shows a definite bias towards the inorganic aspect, primarily because the author's competence and experience originate from this direction.

1.2 THE METHODS OF QUANTITATIVE ANALYSIS

Quantitative analysis, at its inception, dealt almost exclusively with techniques involving gravimetric procedures. These methods, which require the measurement of the weights of known composition products of the analytical process, or the measurement of weight losses or gains associated with such products, include some of the most accurate and precise techniques that the analytical chemist can employ. Many such methods are still applied today, particularly where the demand for accuracy and precision overrides the inherent disadvantages of these methods—disadvantages which include factors such as the relatively long time lapse for a completed procedure, the need for the careful laboratory techniques of the skilled and experienced worker, and the procedural complications often introduced where the substances being analyzed show unusual compositional complexities.

A second group of techniques which appeared shortly thereafter embraced the procedures of volumetric analysis, those covering the standard procedures of volumetric titration applied without the involvement of instrumental methods for the location of the critical point or points of the titration. In this context such methods require the use of prepared titrant solutions of known concentration and the measurement of the volume of such a solution required to react with a given compositional constituent to a specific point, usually the equivalence point, in the titration. Evidence that the critical point is achieved is provided by an indicator reaction that involves a change in a solution characteristic such as color, turbidity,

etc. It should be apparent even at this point that the methods of volumetric analysis have a gravimetric basis, since the preparation of the titrant solution of known composition will nearly always involve at least one accurate weight measurement. The methods of volumetric analysis offer many advantages, not the least of which are the short time lapse to completion for many of the techniques and a somewhat less demanding requirement relative to laboratory manipulative skills.

Over the past 30 years the methods of volumetric analysis have to some considerable extent been subject to a form of instrumentation. By this is meant the increasing use of instrumental techniques, such as the potentiometric, conductometric, amperometric, and absorptiometric techniques, to locate the critical titration point or points or, more generally, to follow the course of the entire titration. In such instances, the volumetric methods are not basically altered from the standard procedures, the instrument functioning as a substitute for some indicator or chemical reaction system for locating a specific titrant volume, such as the equivalence-point volume.

On the other hand, in the past 30 years there has also been an increasing use of what can be described as quantitative analysis performed by instrumental techniques which measure some solution or substance characteristic specifically related directly or indirectly to the concentration of a particular constituent in the substance under investigation. Such techniques include potentiometric, conductometric, coulometric, voltammetric (polarographic), absorptiometric, and fluorometric methods, as well as the methods of flame emission and absorption, emission spectrography, and x-ray emission and absorption spectroscopy. Although such techniques are being applied to a greater and greater extent in the field of industrial and commercial quantitative analysis, it would be a mistake to assume that the standard chemical methods of analysis, such as gravimetric and volumetric methods, will eventually be eliminated from consideration. There are several reasons why this is unlikely ever to occur. First of all, many instrumental methods can not offer the accuracy and precision typical of most chemical methods of analysis. For example, instruments such as the emission spectrograph, the atomic absorption spectrophotometer, and polarographic equipment provide reliable data in the determination of low concentrations of substance constituents but permit only relatively poor accuracy and precision where the higher orders of concentration are involved. Second, such instruments can often be used only after calibration against standard substances whose compositions are accurately known as the result of quantitative analysis by the best of chemical methods of analysis. Third, many instrumental techniques depend, for example, on the measurement of a solution characteristic related to the concentration of a particular constituent, but under conditions where the presence of concentrations of certain other constituents may seriously influence the measurement data secured. In such cases, either chemical methods of separation associated with the general techniques of chemical analysis must be applied in order to eliminate the interfering effects of these constituents or, as is common in many cases of compositional complexity, chemical methods of analysis alone must be applied.

1.3 THE ANALYTICAL CHEMIST AND THE TECHNICIAN

The analytical technician can be considered as someone experienced in laboratory manipulative techniques, capable of following exactly the details of a rigidly defined series of methodic steps in a scheme of chemical or instrumental analysis and able to operate the various instruments used in the modern techniques of quantitative analysis. Such a technician is, in brief, a "cookbook analyst," a term the use of which is not intended to detract in any way from the abilities and value of the analytical technician. The analytical chemist, on the other hand, has an extensive knowledge and understanding of the fundamental principles underlying the methods of chemical and instrumental analysis. He can apply these principles to the modification of existing methods of analysis where required, devise new methods, and adapt developed instrumentation to analytical purposes. He can, where circumstances dictate, devise and modify instrumentation suited to the ends of quantitative analysis. He is fully aware of the limitations imposed by these principles and is prepared to take such limitations into consideration when evaluating the reliability of the analytical data provided by the methods under application.

2
Fundamental Concepts in Quantitative Analysis

2.1 GENERAL

Certain concepts can be considered as fundamental with regard to the principles of quantitative analysis. These include such ideas as solution concentration, chemical equations, chemical equilibrium, stoichiometry, and the basic principles underlying gravimetric, volumetric, and instrumental methods of analysis. In many cases these concepts will receive further detailed treatment in subsequent chapters of the text. The main purpose here is to discuss and review some of the more basic ideas surrounding these concepts.

2.2 SOLUTION CONCENTRATION

The use of solutions in quantitative analysis, whether in association with gravimetric, volumetric, or instrumental methods of analysis, requires that some ba.. for the expression of solution concentration be used in order to indicate the concentration of whatever solute or solutes have been employed. Although all such systems of concentration expression have a fundamentally similar basis with respect to weight relationships of solute and solvent, circumstances often dictate that the actual method of expression take on some convenient and specific form.

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2.2.1 CONCENTRATION AS PERCENT BY WEIGHT

A method of expression of concentration often applied to solutions used in gravimetric work, or in the preliminary procedures of volumetric and instrumental methods, is that of percent by weight. Here the concentration of the solute is expressed as a percentage value representing the grams of solute per 100 g of solution. Thus, the percent by weight for a given solute would be given by

$$P = \frac{W_1}{W_1 + W_2} \, 100$$

where P = percent by weight
   W_1 = weight of solute, g
   W_2 = weight of solvent, g

Where aqueous solutions are involved, since the weight of 1 ml of water at room temperature is approximately 1 g, it is usually quite adequate to substitute for the weight of water in grams the volume in milliliters.

2.2.2 MOLES (MOL) AND EQUIVALENTS

The reactions of chemistry involve atoms, ions, or molecules. The weight of an individual particle is extremely small, and it is impossible for the chemist to consider directly the weight of a single atom, ion, or molecule in reaction. The basis used for considering substances in reaction is the *gram atom*, the *gram ion*, or the *mole*. These units each involve Avogadro's number, 6.023×10^{23}, of particles, so that we have:

One gram atom = the weight in grams of 6.023×10^{23} atoms
   One gram ion = the weight in grams of 6.023×10^{23} ions
      One mole = the weight in grams of 6.023×10^{23} molecules

The tendency exists to refer to the weight in grams of Avogadro's number of any particle as a mole, regardless of the nature of the particle. Thus it is common to find the weight in grams of 6.023×10^{23} Na^+ ions referred to as a mole of Na^+; that of 6.023×10^{23} Cu atoms as a mole of Cu.

The weight in grams of Avogadro's number of the molecules of any compound, it will be remembered, is called the *gram-molecular weight* (GMW), is numerically equal to the *molecular weight*, and can be determined as the *formula weight* of the molecule. Thus the mole is identical in concept to the gram-molecular weight.

Similarly, the weight in grams of Avogadro's number of the atoms of any element is called the *gram-atomic weight* (GAW) and is numerically equal to the *atomic weight*.

Chemical reactions occur on the basis of integral numbers of atoms, ions, or molecules, but these reactions often involve more than just a one-particle-for-one-particle basis. In order to determine the general relationships between substances in chemical reactions, the terms *equivalent* and *equivalent weight* are used. In its

simplest form of expression, the equivalent of an atom, ion, or molecule in reaction is Avogadro's number of electrons, $6.023 \times 10^{23} \, e$.

Example

$H^+ + 1e \rightleftharpoons H$

One mole, or 1.008 g, of hydrogen ions requires 6.023×10^{23} electrons for reduction to hydrogen atoms and is therefore identical to one equivalent of hydrogen ions.
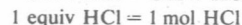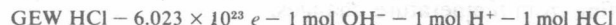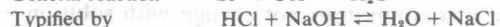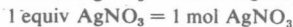
Example

$Cu^{2+} + 1e \rightleftharpoons Cu^+$

One mole, or 63.54 g, of copper (II) ions requires 6.023×10^{23} electrons for reduction to copper (I) ions and is therefore identical to one equivalent of copper(II) ions.

Example

$Cu^{2+} + 2e \rightleftharpoons Cu$
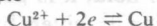
One mole, or 63.54 g, of copper (II) ions requires $2 \times 6.023 \times 10^{23}$ electrons for reduction to copper atoms, and is therefore identical to two equivalents of copper(II) ions.

The *gram-equivalent weight* (GEW) of any substance thus becomes the weight in grams of the atoms, ions, or molecules equivalent in the reaction involved to Avogadro's number of electrons, and it is numerically equal to the equivalent weight. Thus, in the examples just given, the equivalent weight of hydrogen is 1.008, that of copper in the first copper reaction is 63.54, and that of copper in the second copper reaction is 31.77. It is important to note that the equivalent weight of an atom, ion, or molecule is directly related to the reaction in which it is involved, and that it is entirely possible for a substance to show more than one equivalent or equivalent-weight value.
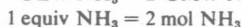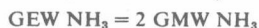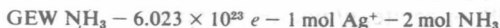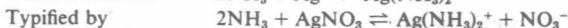
Example

General reaction $H^+ + OH^- \rightleftharpoons H_2O$
Typified by $HCl + NaOH \rightleftharpoons H_2O + NaCl$

GEW HCl $- 6.023 \times 10^{23} \, e - 1$ mol $OH^- - 1$ mol $H^+ - 1$ mol HCl

GEW HCl = GMW HCl
1 equiv HCl = 1 mol HCl

Example

General reaction $Ag^+ + Cl^- \rightleftharpoons AgCl(s)$
Typified by $AgNO_3 + HCl \rightleftharpoons AgCl(s) + HNO_3$

GEW $AgNO_3 - 6.023 \times 10^{23} \, e - 1$ mol $Cl^- - 1$ mol $Ag^+ - 1$ mol $AgNO_3$

GEW $AgNO_3$ = GMW $AgNO_3$
1 equiv $AgNO_3$ = 1 mol $AgNO_3$

Example

General reaction $2NH_3 + Ag^+ \rightleftharpoons Ag(NH_3)_2^+$
Typified by $2NH_3 + AgNO_3 \rightleftharpoons Ag(NH_3)_2^+ + NO_3^-$

GEW $NH_3 - 6.023 \times 10^{23} \, e - 1$ mol $Ag^+ - 2$ mol NH_3

GEW NH_3 = 2 GMW NH_3
1 equiv NH_3 = 2 mol NH_3

Example

$$K_2Cr_2O_7 + Pb(NO_3)_2 \rightleftharpoons PbCr_2O_7(s) + 2KNO_3$$
$$GEW\ K_2Cr_2O_7 = GMW/2\ K_2Cr_2O_7$$
$$1\ equiv\ K_2Cr_2O_7 = \tfrac{1}{2}\ mol\ K_2Cr_2O_7$$

Example

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \rightleftharpoons 2CrCl_3 + 6FeCl_3 + 2KCl + 7H_2O$$
$$GEW\ K_2Cr_2O_7 = GMW/6\ K_2Cr_2O_7$$
$$1\ equiv\ K_2Cr_2O_7 = \tfrac{1}{6}\ mol\ K_2Cr_2O_7$$

2.2.3 CONCENTRATION AS MOLALITY

In disciplines such as physical chemistry, solution concentration is often expressed as *molality*. Although rarely used in the analytical field, it is perhaps worthwhile to consider it briefly. The molality of a solution is given by the number of moles of solute per 1000 g of solvent, and we have

$$m = \frac{W_1}{(MW)(W_2)}\ 1000$$

where m = molality
      W_1 = weight of solute, g
      MW = molecular weight of solute, g/mol
      W_2 = weight of solvent, g

Example 28.00 g of NaOH is dissolved in 3500 g of water at 25°C. Determine the molality at 25°C in terms of NaOH.

$$m = \frac{28.00}{40.00 \times 3500}\ 1000 = 0.2000$$

Note that the molality of a solution does not change with solution volume changes resulting from temperature changes.

2.2.4 CONCENTRATION AS MOLARITY

One of the important methods of solution-concentration expression used in the field of quantitative analysis is that of *molarity*. The molarity of a solution is given by the number of moles of solute per liter of solution. Since the millimole is one-thousandth of a mole and the milliliter is one-thousandth of a liter, we can use the expression

$$M = \frac{W_1}{(MW)(V)}$$

where M = molarity
      W_1 = weight of solute, g or mg
      MW = molecular weight of solute, g/mol, or mg/mmol
      V = volume of solution, l, or ml

Since molarity involves a basis of solution volume, it is apparent that the molarity of a solution will change with volume changes associated with changes in temperature. Thus, a solution prepared as 0.1000 M at 25°C will show a molarity somewhat less than this value at, for example, 50°C.

2.2.5 CONCENTRATION AS FORMALITY

Many substances do not exist in the molecular form, whether in the solid or the solution state. Salts such as NaCl and $FeCl_3$ maintain the ionic form (Na^+ and Cl^-, Fe^{3+} and Cl^-) in the solid state as well as in aqueous solution. The preparation, for example, of a 1-M solution of $FeCl_3$ has thus no logical basis, since the molecular form of $FeCl_3$ does not exist from start to finish of the preparation procedure. Many chemists have therefore insisted that the *formula weight*, rather than the molecular weight, be used in the preparation of solutions, and that the solution concentration then be expressed in *formality*. On this basis one defines formality as being the number of formula weights of a solute per liter of solution. Thus we have

$$F = \frac{W_1}{(FW)(V)}$$

where F = formality
W_1 = weight of solute, g
FW = formula weight of solute, grams per formula
V = volume of solution, l

Example 16.22 g of $FeCl_3$ is dissolved in water and diluted to exactly 1000 ml at 25°C. What is the formality of this solution? What is its molarity in terms of Fe^{3+} and in terms of Cl^-?

$$F = \frac{16.22}{162.21 \times 1.000}$$
$$= 0.1000$$
$$M \text{ as } Fe^{3+} = 0.1000$$
$$M \text{ as } Cl^- = 0.3000$$

Again, because of the volume basis of preparation, formal solutions will show changes in formality with volume changes associated with temperature changes. There is a certain logic where this method of concentration expression is concerned, but in this text, we shall continue to use the molar method of expression as being entirely satisfactory in its application to analytical chemistry.

2.2.6 CONCENTRATION AS NORMALITY

The *normality* of a solution is given by the number of equivalents of solute per liter of solution. It is emphasized most strongly that since the equivalent or equivalent weight of a substance may vary according to the reaction in which it is in-

volved, the use of the normality as a means of expressing a solution concentration should *always* be accompanied by a reference to the associated reaction or the associated molarity.

Since the milliequivalent is one-thousandth of an equivalent, we can use

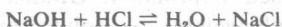$$N = \frac{W_1}{(EW)(V)}$$

where N = normality
W_1 = weight of solute, g, or mg
EW = equivalent weight of solute, g/equiv, or mg/mequiv
V = volume of solution, l, or ml

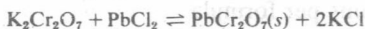The numerical value of EW in each equation is, of course, identical.

Example NaOH in the reaction
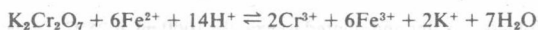
$$NaOH + HCl \rightleftharpoons H_2O + NaCl$$

has an equivalent weight of 40.00. 5.00 g of NaOH is dissolved in water and the solution diluted to exactly 500 ml at 25°C. Determine the normality in terms of NaOH.

$$N = \frac{5.00}{40.00 \times 0.500} = 0.2500$$

Example $K_2Cr_2O_7$ in the reaction

$$K_2Cr_2O_7 + PbCl_2 \rightleftharpoons PbCr_2O_7(s) + 2KCl$$

has an equivalent weight of 147.10, and in the reaction

$$K_2Cr_2O_7 + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 2K^+ + 7H_2O$$

it has an equivalent weight of 49.03.

24.52 g of $K_2Cr_2O_7$ is dissolved in water and diluted to exactly 1000 ml at 25°C. Determine the normality of this solution in terms of $K_2Cr_2O_7$ for each reaction.

Reaction with $PbCl_2$: $N = \dfrac{24.52}{147.10 \times 1.000} = 0.1667$

Reaction with Fe^{3+}: $N = \dfrac{24.52}{49.03 \times 1.000} = 0.5001$

Note that the *same* solution has *two* normality values, and that confusion could easily arise when the expression of normality is *not* accompanied by the associated reaction identification or some other positive method of relating normality to solution usage.

Here again, because of the volume basis of preparation, normal solutions will show changes in normality with volume changes associated with changes in temperature.

It is important to note the rather obvious fact that the equivalent weight and the molecular weight are related by the equation

$$EW = \frac{MW}{n}$$